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THE FRACTURE OF THERMOSETTING RESINS AFTER EXPOSURE TO WATER. (U)

SEP 80 G PRITCHARD, R G ROSE

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AFTER EXPOSURE TO WATER.

by

Geoffrey Pritchard

R.G. / Rose

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# THE FRACTURE OF THERMOSETTING RESINS

## AFTER EXPOSURE TO WATER

### S U M M A R Y

Advanced composite materials should be able to withstand hot, wet conditions. This investigation is concerned with organic, cross-linked resins and specifically with unsaturated polyester resins. The aim was to determine the extent of loss of fracture toughness of the unreinforced resins as a result of immersion in hot water. Data are presented for one polyester resin, immersed in water at 30°C and at 65°C for nearly two years. A theory of degradation is outlined. The findings are currently being extended to a series of resins differing only in molecular weight distribution and in number-average molecular weight. The outcome should be the establishment of optimum molecular weight distributions.

Keywords - Polyester resin, fracture toughness,  
water, embrittlement, molecular weight,  
osmosis, hydrolysis.

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## THE FRACTURE OF THERMOSETTING RESINS

### AFTER EXPOSURE TO WATER

#### 1. THE PROBLEM

This project attempts to establish how far a resin matrix can become embrittled by treatment with warm water. The term "embrittled" means in this context that the fracture toughness is lowered and crack growth facilitated.

Fibre-resin composites are widely used in moist environments and their mechanical properties are known to deteriorate as a result of exposure to hot, wet conditions (1-4). This is not necessarily because of matrix damage. There is much to be said for the view that hot water attacks fibre-resin composites by inducing or enlarging flaws in the glass reinforcement (5). But this process would certainly be accelerated by the development of diffusion pathways through resin microcracks, if these were induced during service life. In any case, the mechanical properties of fibre-resin composites cannot be independent of matrix toughness. Anything which facilitates crack propagation in the matrix affects composite behaviour adversely.

The experimental work falls into two distinct, but related parts. The first stage is now complete. This was to determine the effect on matrix toughness of prolonged immersion in water at 65°C. The resin was studied in absence of glass reinforcement, to isolate resin-related processes. In order to understand the effect of water immersion better, the resin was also immersed in certain other aqueous liquids. At the time of commencement of U.S. Army support, this first stage was well advanced towards completion; it involved a single batch of factory-made isophthalic polyester resin, of the kind used in filament-wound pipe. This part of the work will be referred to as the isophthalic programme.

The second stage was to determine how far the behaviour of a polyester resin in warm water depended on "fine tuning" of the resin structure. Most resins are described in the scientific literature simply by the chemicals used to produce them. These are certainly important; for example, resins made from isophthalic acid are known to be more water-resistant than those made from the orthophthalic isomer. But why? It has been suggested that the only reason is the tendency for isophthalic resins to have higher molecular weights. Certainly the molecular weight has an effect on water resistance (6), but it is not certain whether this is a function of the number of chain ends or of the total distribution of chain lengths.

Recently, the development and widespread adoption of the technique of gel permeation chromatography (GPC) has enabled chemists to describe resins in terms of molecular weight distribution and the time seemed opportune to establish an optimum distribution for the retention of mechanical properties in water. Therefore the second stage of the work described here was concerned with synthesizing a whole series of resins, all having the same nominal composition, but actually differing in molecular weights and molecular weight distributions. Such a project requires analysis to provide confirmation of the detailed structure of the resins, after which their retention of fracture toughness in hot water is to be assessed.

This series of resins is now being prepared from the same formulation as the first resin, except that orthophthalic rather than isophthalic acid is employed. As a result, this section will be designated the orthophthalic programme.

The report describes the isophthalic programme, now completed, and indicates the nature of the orthophthalic programme (still at an early stage - no results are yet available).

## 2. BACKGROUND

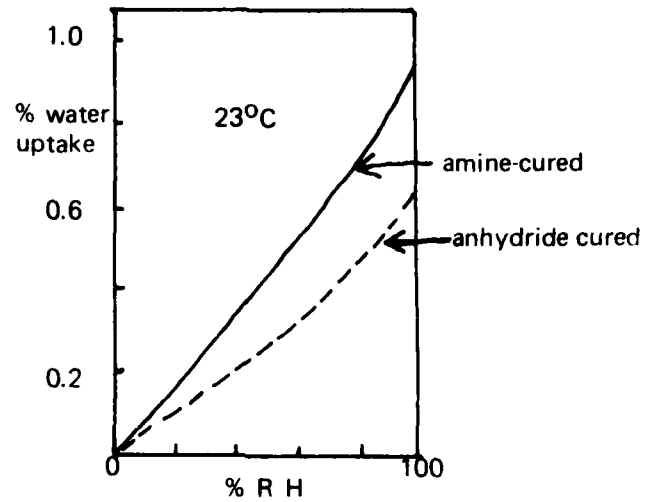
### 2.1 Thermosetting resins

Thermosetting resins are crosslinkable, usually organic polymers. Examples are the phenol-formaldehyde, urea-formaldehyde and melamine-formaldehyde resins, epoxides, unsaturated polyesters, diallyl phthalate resins, furanes and certain kinds of polyimides. Their chief characteristics are that in the finished state they are (i) insoluble and (ii) infusible. They often show notch sensitivity. Practical applications require that the resins are reinforced, unless their use is for coatings, adhesives or purely decorative mouldings.

Another distinctive feature of the resins listed above is that they contain water-attracting chemical groups, such as carbonyl, ether bridges, ester links and amine groups. The water resistance of thermosetting resins is therefore not ideal. Even as composites containing 70% w/o inorganic fibre, the best epoxide materials absorb more than 1% w/w of water at equilibrium. (See Figure 1).

Most recent studies of the effect of water on thermosetting resins have been related to epoxides (7-9). The results of these investigations are summarised by Morgan and O'Neal (10) and by Morgan, O'Neal and Fanter (11). However, there are many questions of controversy arising from such investigations. The above authors' contention that crosslinked polymers fail by a crazing mechanism not unlike that found in glassy thermoplastics, is disputed. The tendency to craze is said by those who postulate it to enhance the accessibility of moisture to sorption sites and to advance the moisture-induced degradation of crosslinked polymers.





bisphenol cured epoxy/glass  
laminate  
( $V_F = 0.55$ )

Source: H W Gitschner and G Menges  
(Aachen, W. Germany)

Fig. 1

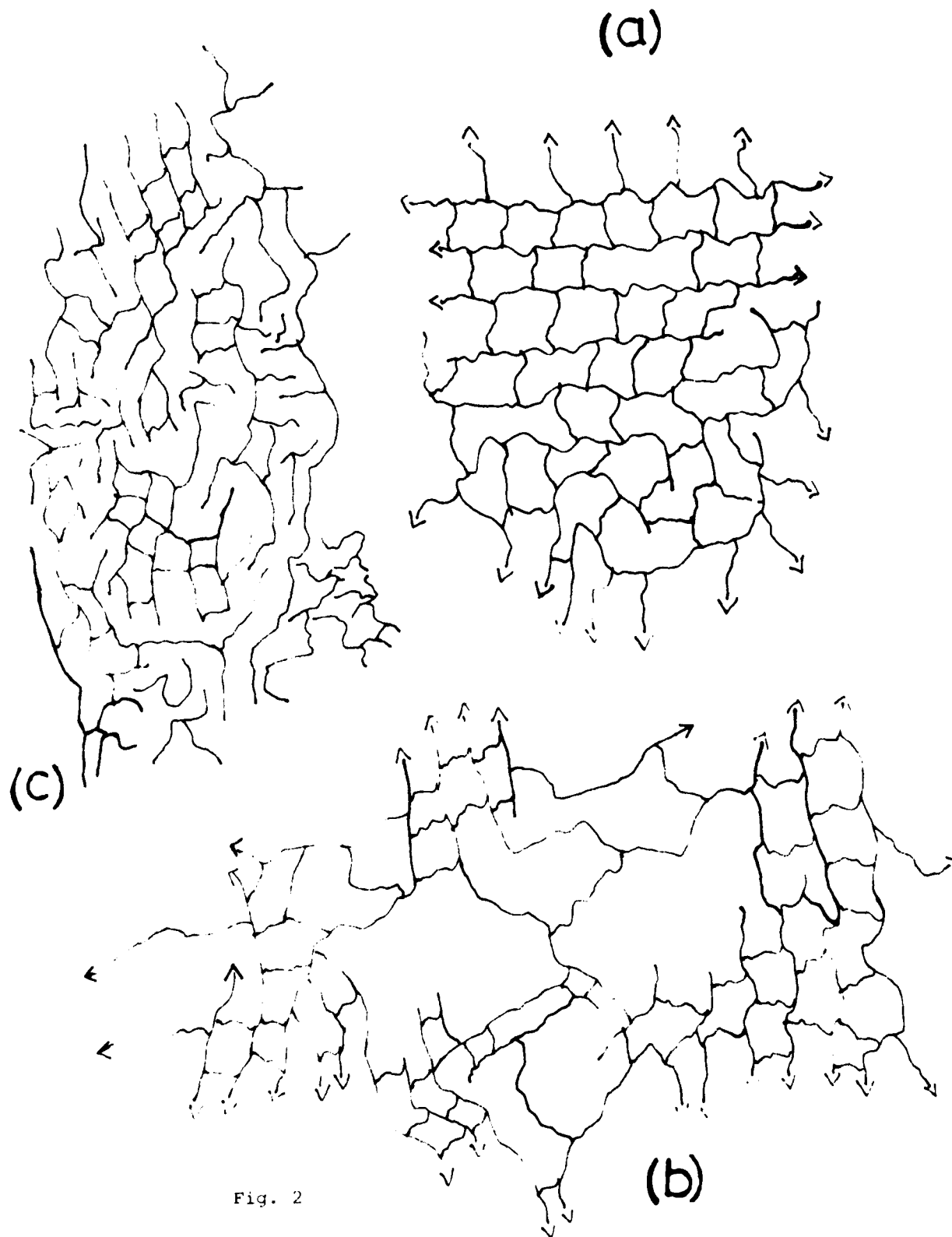


Fig. 2

Another area of uncertainty is the supermolecular structure of crosslinked resins. The uncertainty arises because chemical and physical characterization methods are difficult to apply to such intractable materials. Figure 2 shows three possible structures of thermosetting resins. A uniform density of continuous network structure is shown in Figure 2 (a), while an agglomeration of cross-linked material is shown in Figure 2 (b). The third representation 2 (c), shows discrete micelles of crosslinked network, unconnected by any covalent bonds, but probably held together by physical entanglements which are not shown in the Figure. Present opinions virtually rule out 2 (a), but the exact nature of thermosetting networks is still unconfirmed. Probably a structure intermediate between (b) and (c) corresponds most closely with reality.

This question is important when considering the deformation of thermosetting resins under load. It seems likely that molecular flow occurs at crack tips and this capacity for flow has to be reconciled with the known three-dimensional network structure of these materials.

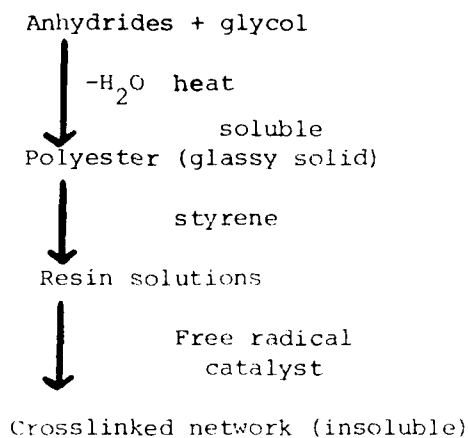
## 2.2 Unsaturated polyesters

Unsaturated polyester resins are widely used in contact with moisture, notably in marine, chemical process, pipe and food storage applications. Like epoxides, these resins withstand water well, except at higher temperatures. The reason for their susceptibility to hot water is generally thought to be the breaking of chain segments by hydrolysis of ester groups, i.e. by reversal of the process leading to the synthesis of these resins. Figure 3 indicates how a resin is synthesized and subsequently crosslinked by styrene.

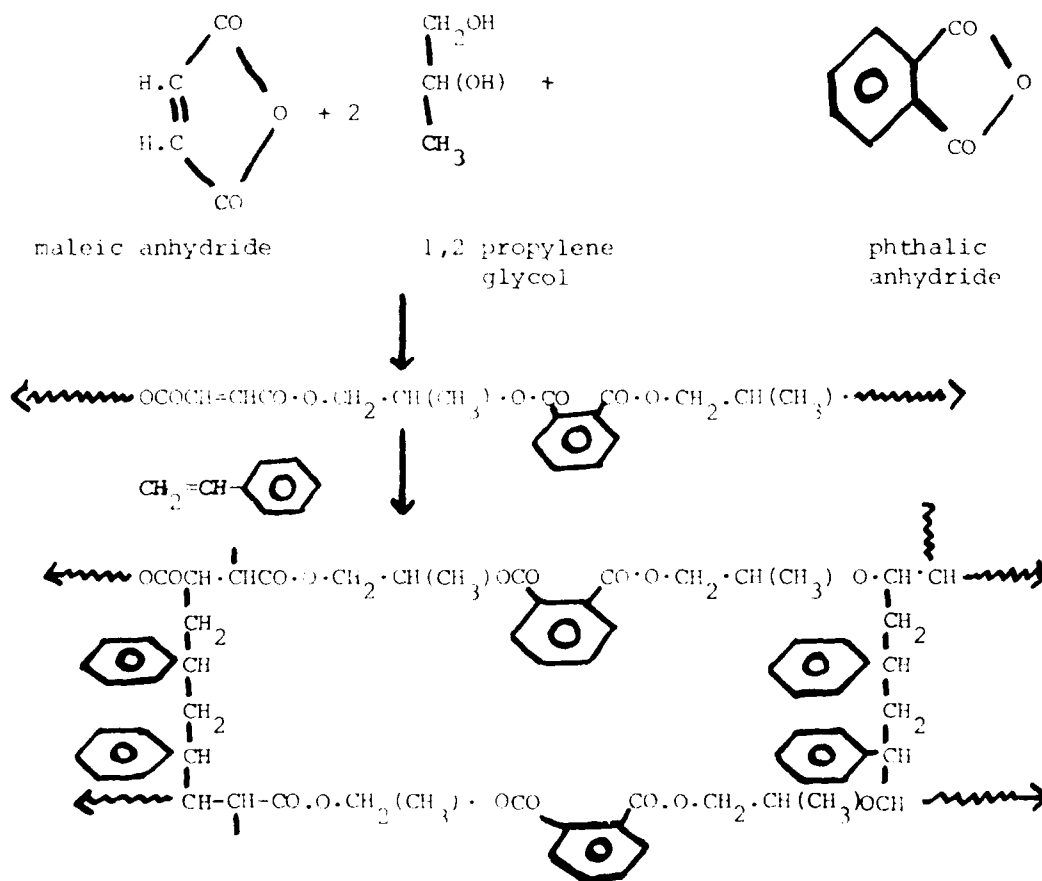
Referring to Figure 3, i.e. the final crosslinked network, it should be noted that the distribution of phthalic and maleic groups in the polyester backbone is not necessarily regular and the number of styrene molecules incorporated into the bridges is not necessarily two; this is an average (12). The length of the ester-containing chains is fairly short (number-average molecular weight about 1000 to 2000) while the length of the crosslinking chains containing styrene is said to be much longer, with number-average molecular weight between 8000 and 14,000.

Common polyester resins are made by heating together the chemicals mentioned above, typically at about 190°C for about 8-20 hours, depending on the chain length desired. The chief variations in synthetic procedure are (a) replacement of phthalic anhydride by isophthalic acid and (b) use of different glycols. Different proportions of unsaturated (maleic) to aromatic (phthalic or isophthalic) component can also be used. (13)

FIGURE 3



Example



### 2.3 Fracture toughness of polyesters

The fracture toughness of materials may be expressed in several ways. The Griffith approach (14) explained the relatively low strength of a brittle solid by the presence of flaws; he related the tensile fracture stress,  $\sigma_f$ , of a specimen containing an elliptical through-thickness centre crack of length  $2a$ , to the Young's modulus  $E$  and surface energy  $\gamma$  of the solid, by the equation

$$\gamma = \frac{1}{2} \frac{\sigma_f^2 \cdot \pi a}{E} \quad (1)$$

This equation assumes plane stress loading. For plane strain,

$$\gamma = \frac{1}{2} \cdot \frac{\sigma_f^2 \cdot \pi a(1-\mu^2)}{E} \quad (2)$$

Later, it was established that the energy absorbed by plastic deformation near the crack tip vastly exceeds the fracture surface energy, so  $\gamma$  was replaced by  $\gamma_p$ , the energy absorbed by plastic deformation during the creation of unit area of fracture surface. The quantity  $G_c (=2\gamma_p)$  is the strain energy release rate and so

$$\sigma_f = \left( \frac{G_c E'}{\pi a} \right)^{1/2} \quad (\text{plane stress}) \quad (3)$$

or

$$\sigma_f = \left( \frac{G_c E}{\pi a(1-\mu^2)} \right)^{1/2} \quad (\text{plane stress}) \quad (4)$$

Experimentally determined values of  $\gamma_p$  for a few unsaturated polyester resins have been reported (15).

The Griffith approach does not explain the time-dependent nature of failure in polymers (16) nor does it help the study of how  $\gamma_p$  depends on crack velocity (17). The alternative, stress distribution approach to the study of brittle fracture utilizes a parameter  $K$ , known as the stress intensity factor, such that

$$K^2 = Y \sigma^2 a \quad (5)$$

$Y$  is a geometrical factor.  $K$  rises during the application of increasing loads to a magnitude  $K_c$  at which fracture occurs; i.e.

$$K_c^2 = Y \sigma_f^2 a$$

When the tensile opening mode of fracture is employed,  $K_{IC}$  and  $G_{IC}$  are called  $K_{IC}$ ,  $G_{IC}$ . Specimen geometries used with thermosetting resins include the single edge notched (18), the three-point bending (19), double torsion (20), double cantilever beam (21), tapered double cantilever beam (22), compact tension (23) and centre notched (24).

Some of these specimen geometries allow good control over the rate of crack propagation and so  $K_{IC}$  can be measured as a function of crack velocity. However, in the present programme the last-named centre-notched variety was the principal form adopted, partly because of the large number of specimens to be made and exposed in liquids, but also to correlate results with previously obtained data. The tapered double cantilever beam geometry has been shown to give similar results to those obtained from "unstable" geometries such as the single edge notched specimens (21).

Most unsaturated polyester resins, but not all, have substantially linear-elastic stress-strain curves up to the point of fracture, at least at ambient temperatures (25). This is certainly true of polyester resins made from the starting materials mentioned in the previous section, provided that the molar ratio of maleic:phthalic is at least 1:2.

Pritchard, Rose and Taneja (18) reported a value of  $0.84 \text{ MNm}^{-3/2}$  for  $K_{IC}$  of a highly crosslinked polyester resin, using single-edge notched specimens. Owen and Rose (24) obtained values in the range  $0.66\text{--}2.16 \text{ MNm}^{-3/2}$  for a variety of "flexibilised" polyesters, using the centre-notched geometry.

#### 2.4 Fractography of Polyesters

The use of scanning electron microscopy is now a standard technique for the examination of fracture surfaces of polymers. At the higher magnifications the electron beam can damage the specimen surface, but in general, lower magnifications, to show the overall structure, are used. A review of published information (26) on the morphology of fracture surfaces of highly cross-linked resins indicates there is little information about polyesters. Most of the work relates to glassy thermoplastics, cross-linked phenol-formaldehyde (27) and epoxy resins (22), but some work on the fracture surfaces of polyesters with varying flexibiliser additions has been reported (28).

When fracture occurs below the glass transition temperature, the mechanism of crack propagation and the associated morphology of the fracture surfaces appears to be influenced by the degree of cross-linking. Morgan et al. (11) observed cavities and fractured fibrils in non cross-linked glasses and lightly cross-linked epoxies near the crack initiation site and these features were associated with

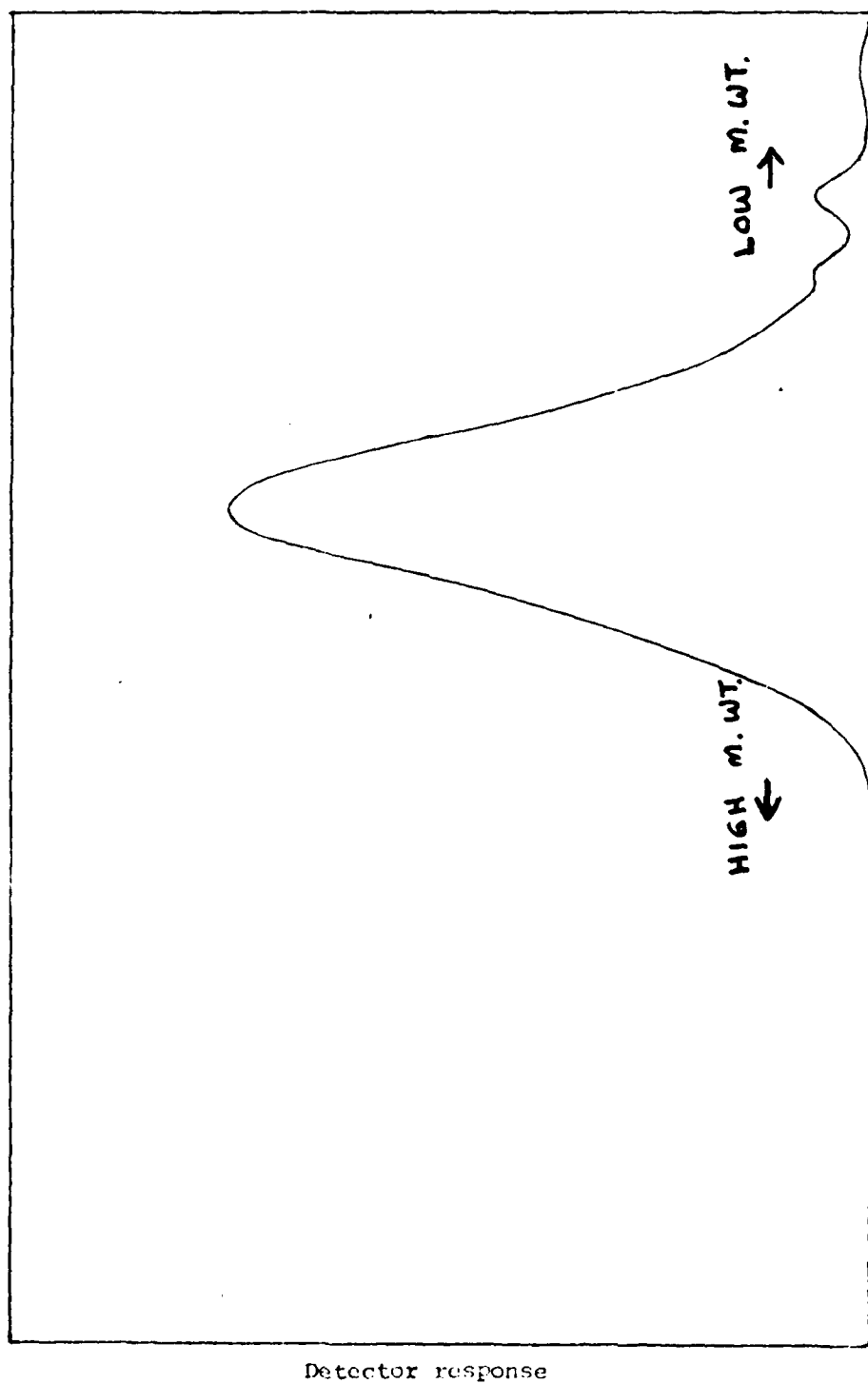
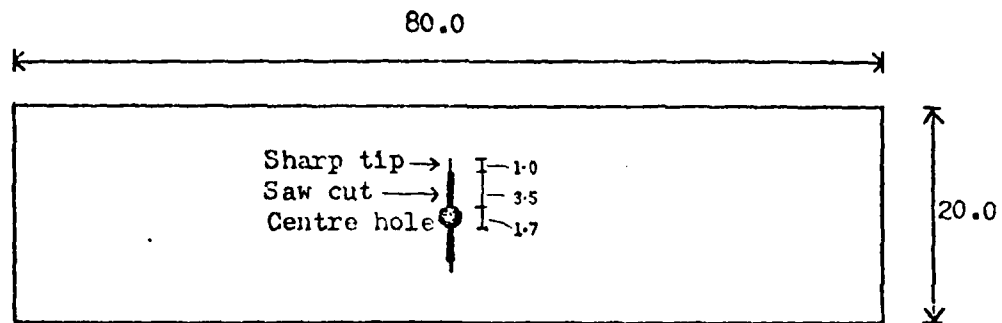


Fig. 4 Molecular weight distribution of the polyester.

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All dimensions in mm

Fig. 5

Centre-notched fracture toughness test piece.



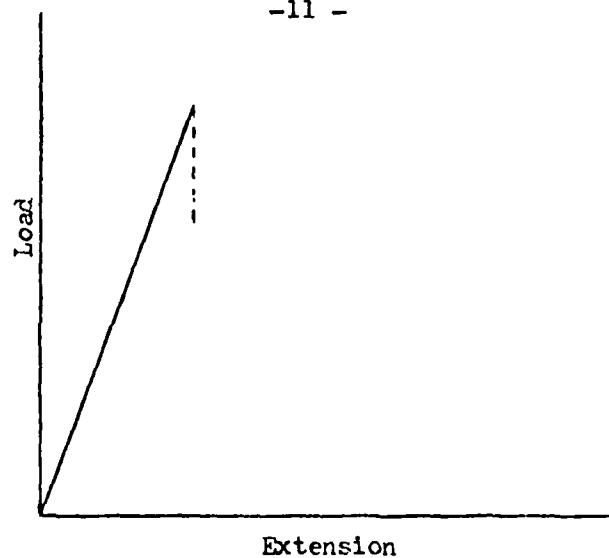


Fig. 6a

Load-extension curve for centre-notched test pieces under uniaxial tension

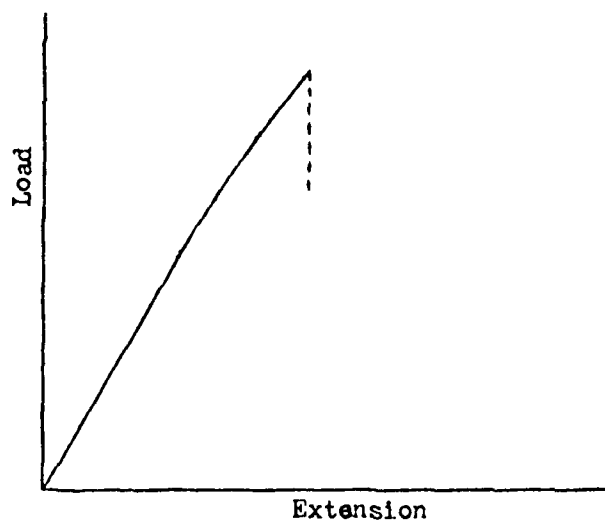


Fig. 6b

Load-extension curve for tensile dumbbells under uniaxial tension.

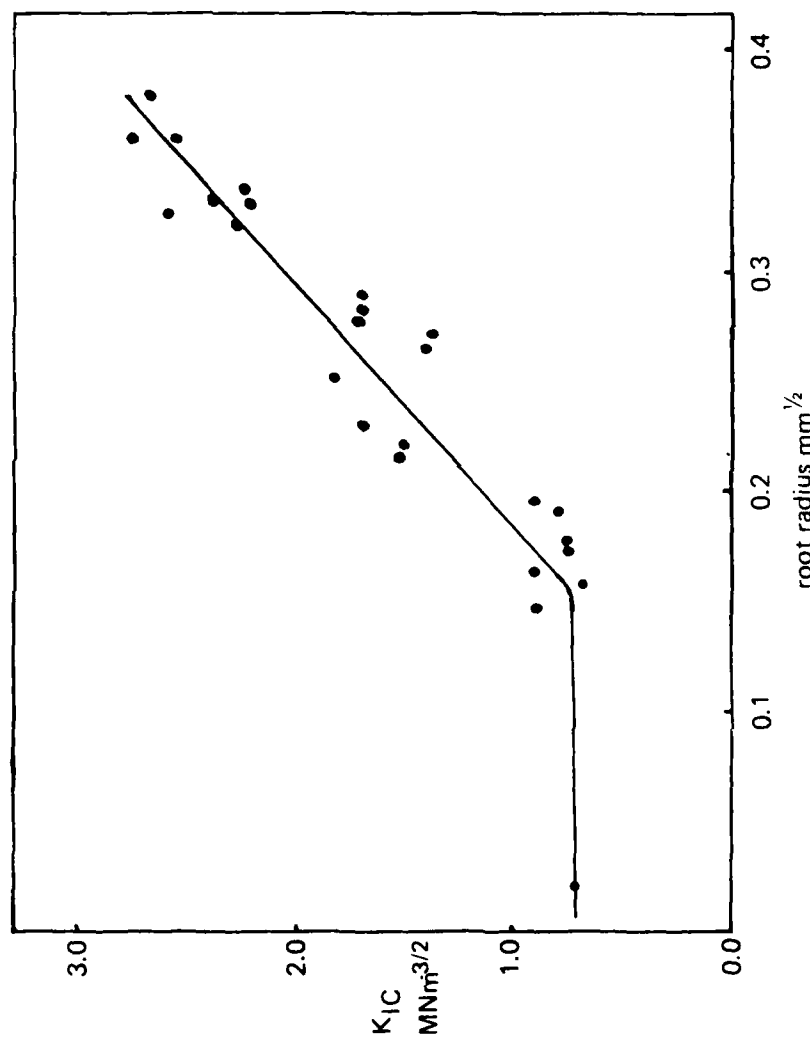


Fig. 7 Change in  $K_{IC}$  with crack tip radius

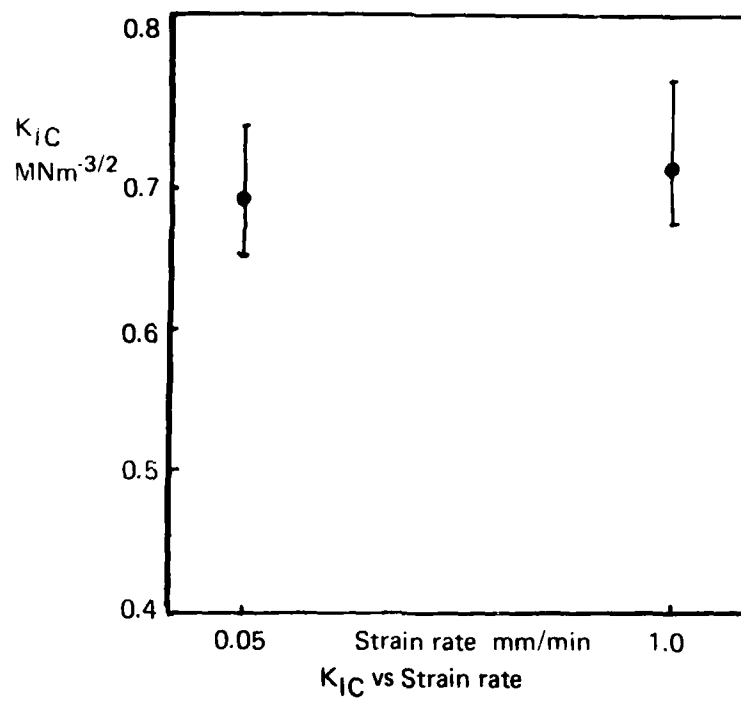


Fig. 8

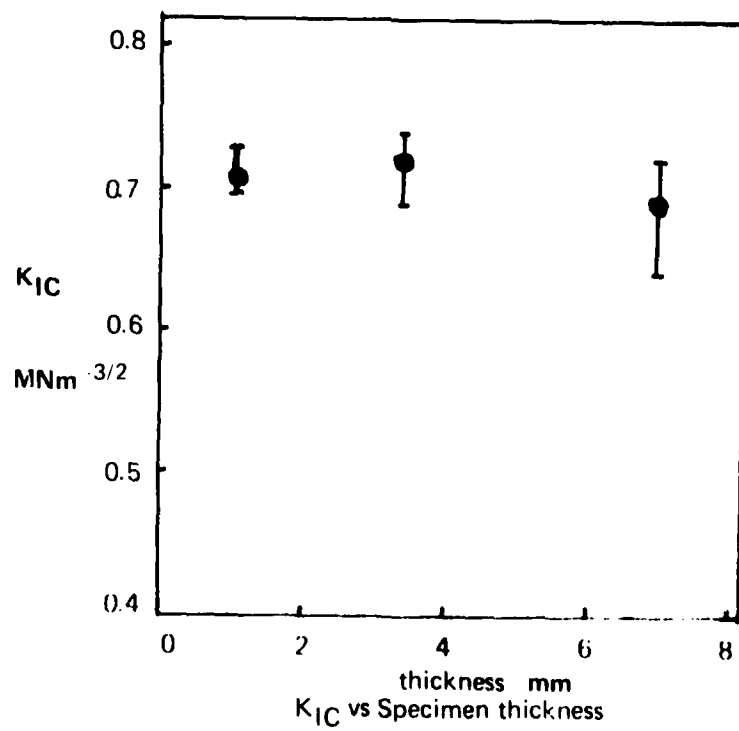


Fig. 9

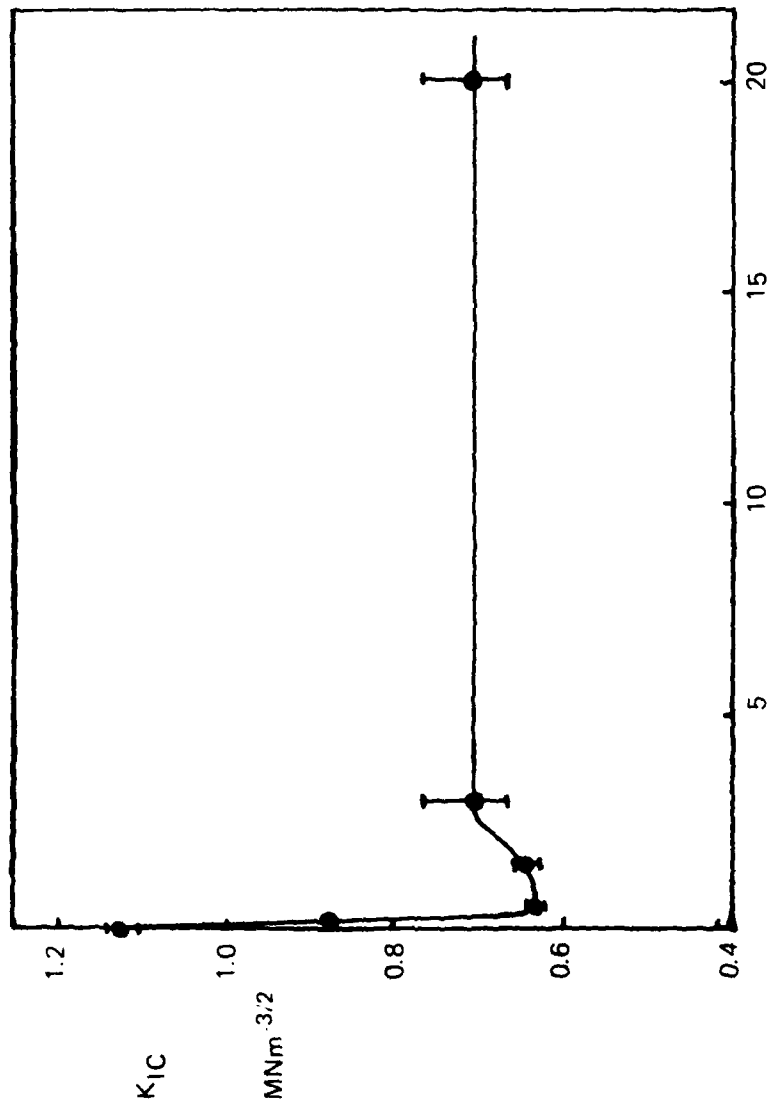


Fig. 10 Change in  $K_{IC}$  with post-cure time at  $80^\circ\text{C}$

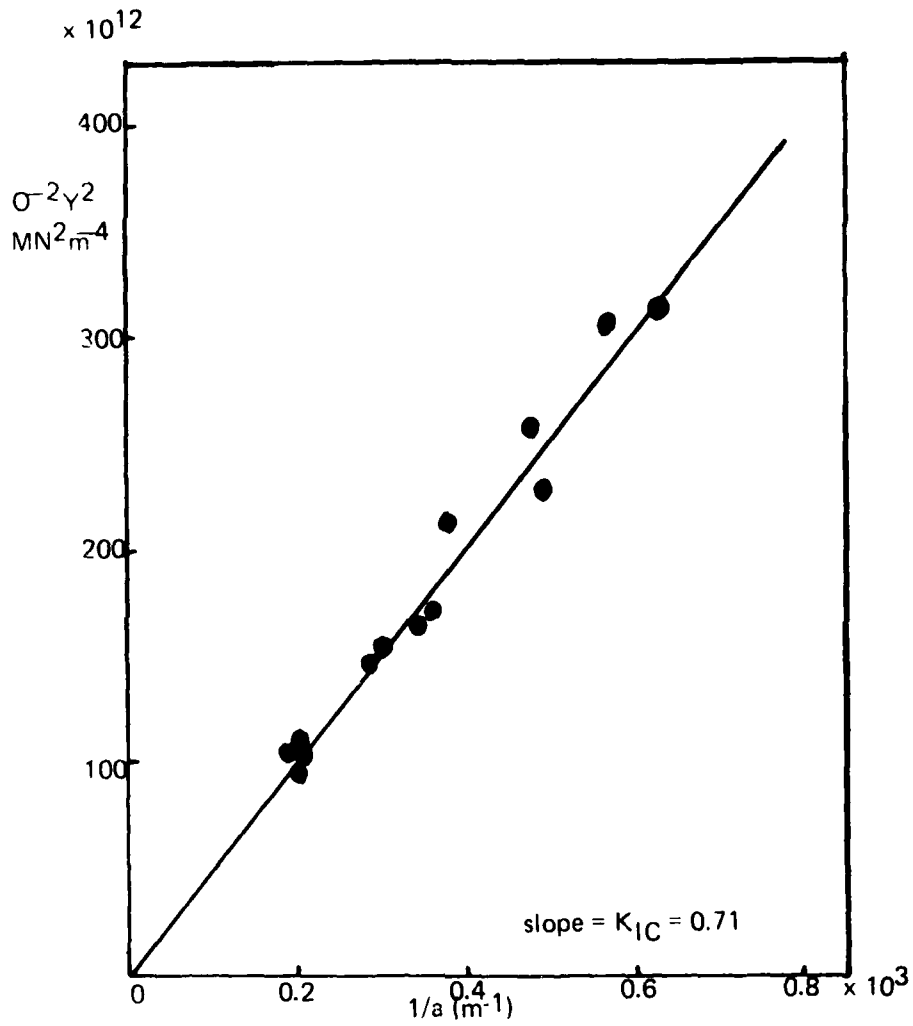
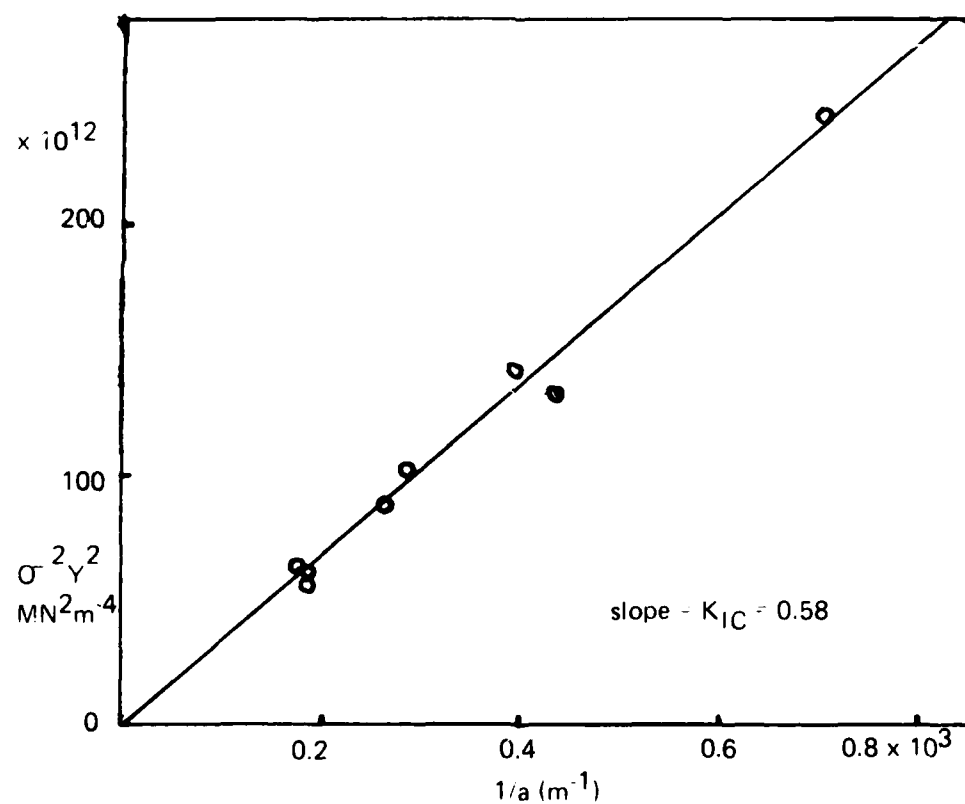


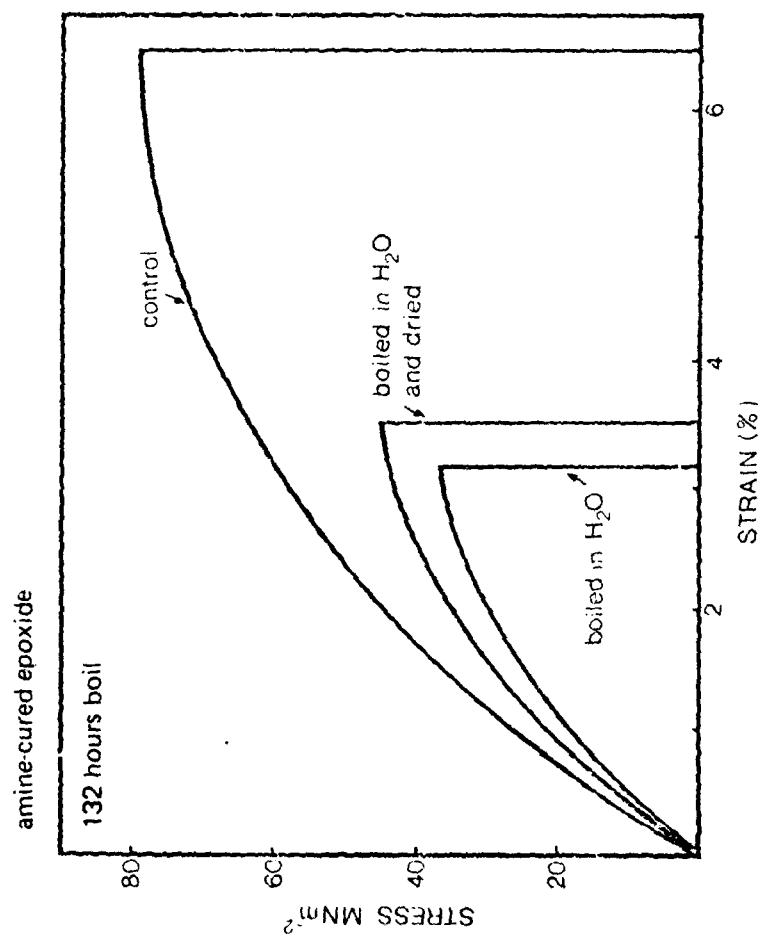
Fig. 11

$\sigma^2 \gamma^2$  vs  $1/a$  for the unimmersed resin



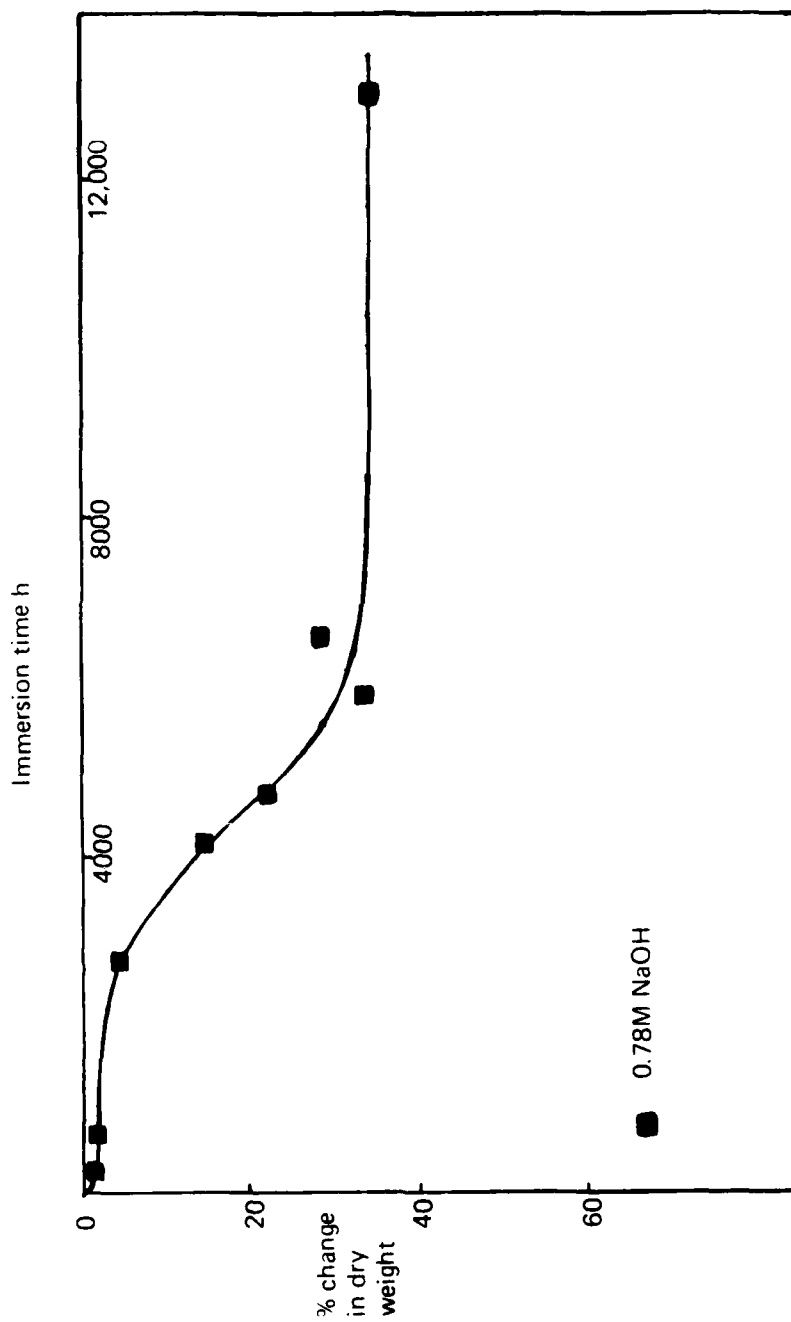
$\sigma_Y^2$  vs  $1/a$  for the immersed resin (in  $\text{H}_2\text{O}$ , 3000 h at  $65^\circ\text{C}$ )

Fig. 12



Ref: D H Kaelble and P J Dynes  
J Adhesion, 8, (1977) 195

Fig. 13



Change in dry weight with immersion time at 65°C

Fig. 14



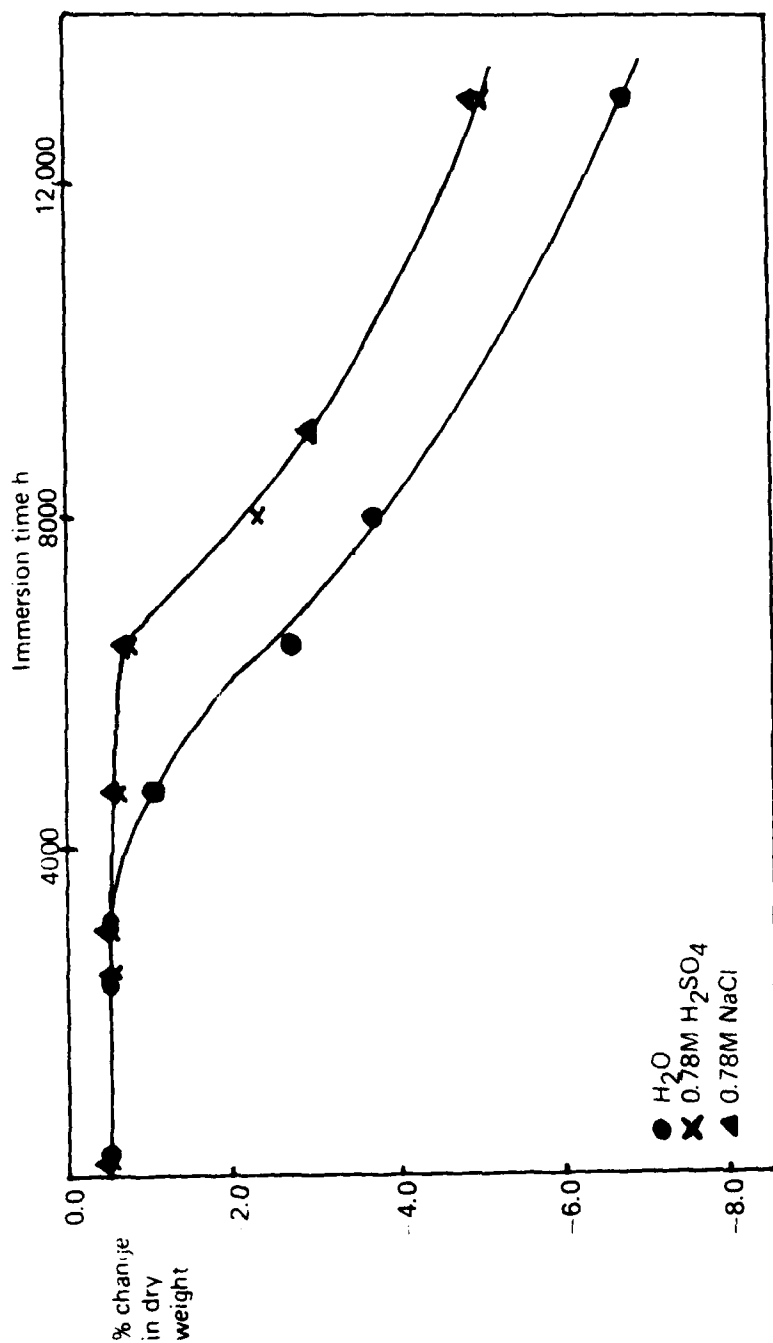
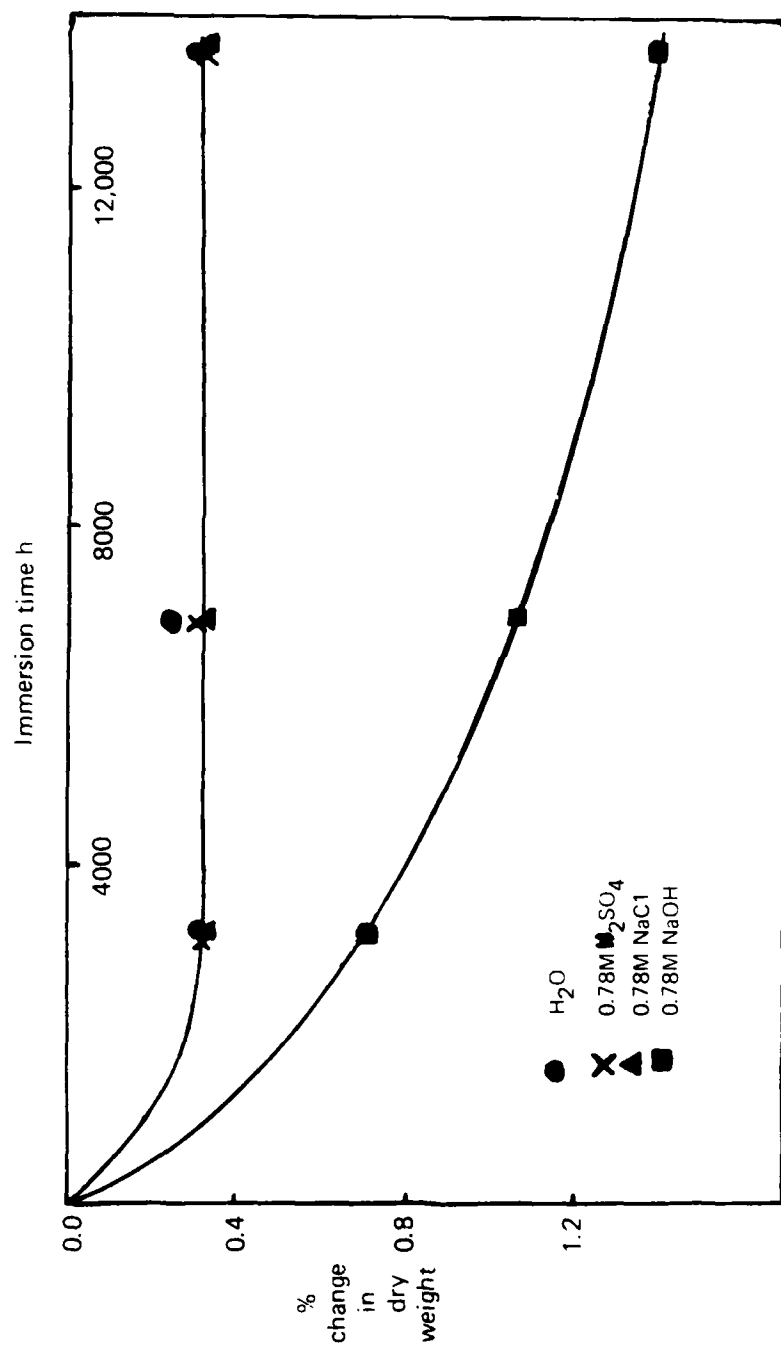


Fig. 15 Change in dry weight with immersion time at 65°C



Change in dry weight with immersion time at 30°C

Fig. 16

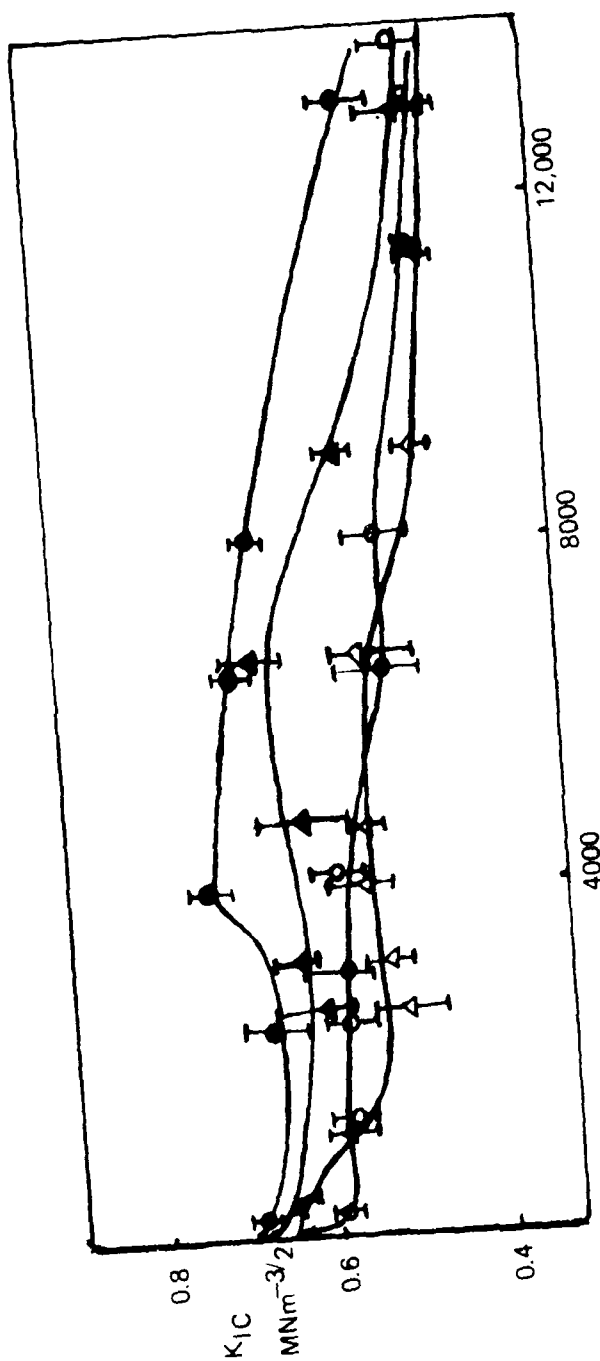


Fig. 17 Immersion Time (Hours)  
Change in  $K_{IC}$  with Immersion Time at 65°C

Wet Dry  
 $\circ$   $\bullet$   $H_2O$   
 $\triangle$   $\blacktriangle$  0.78 m NaCl

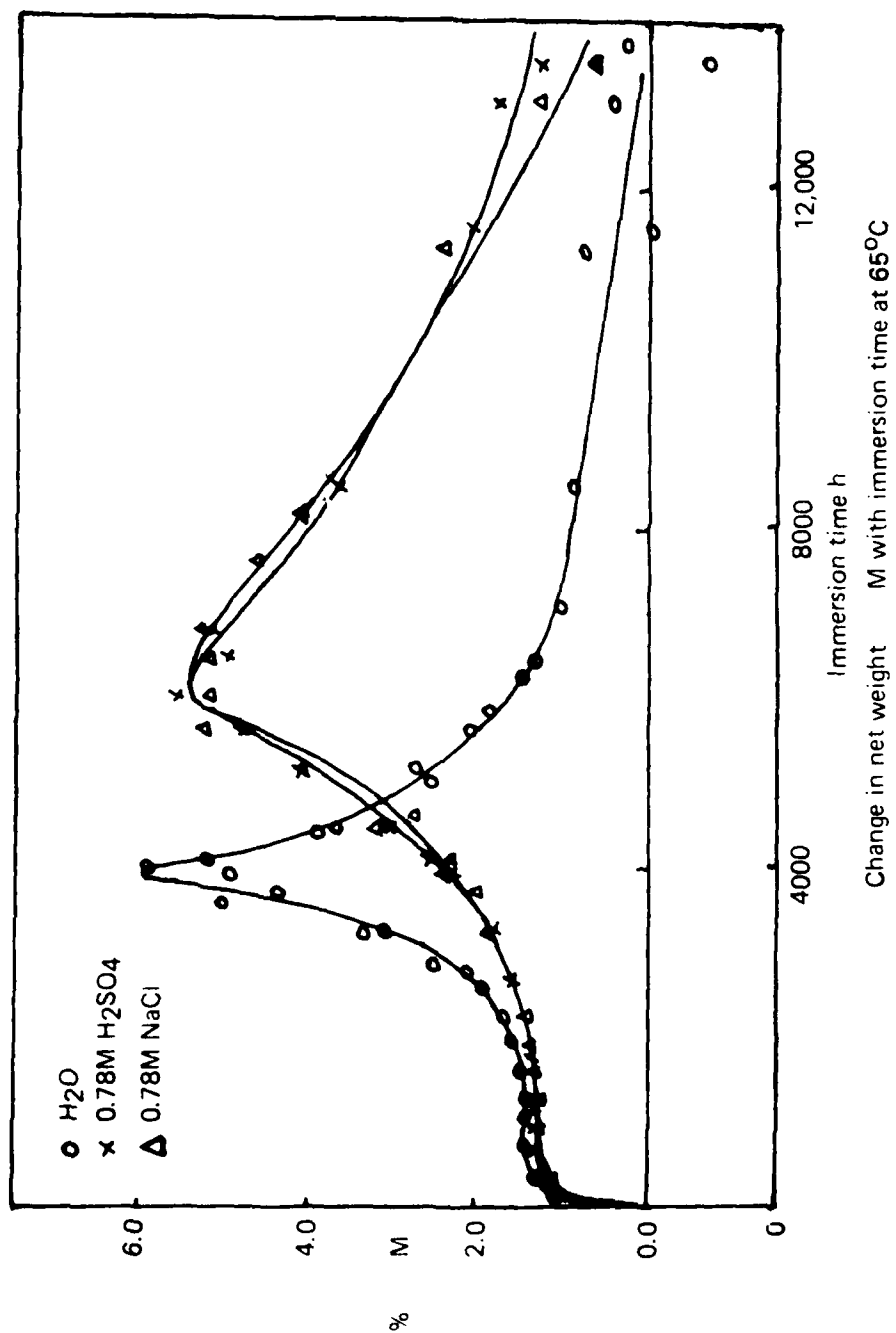


Fig. 18

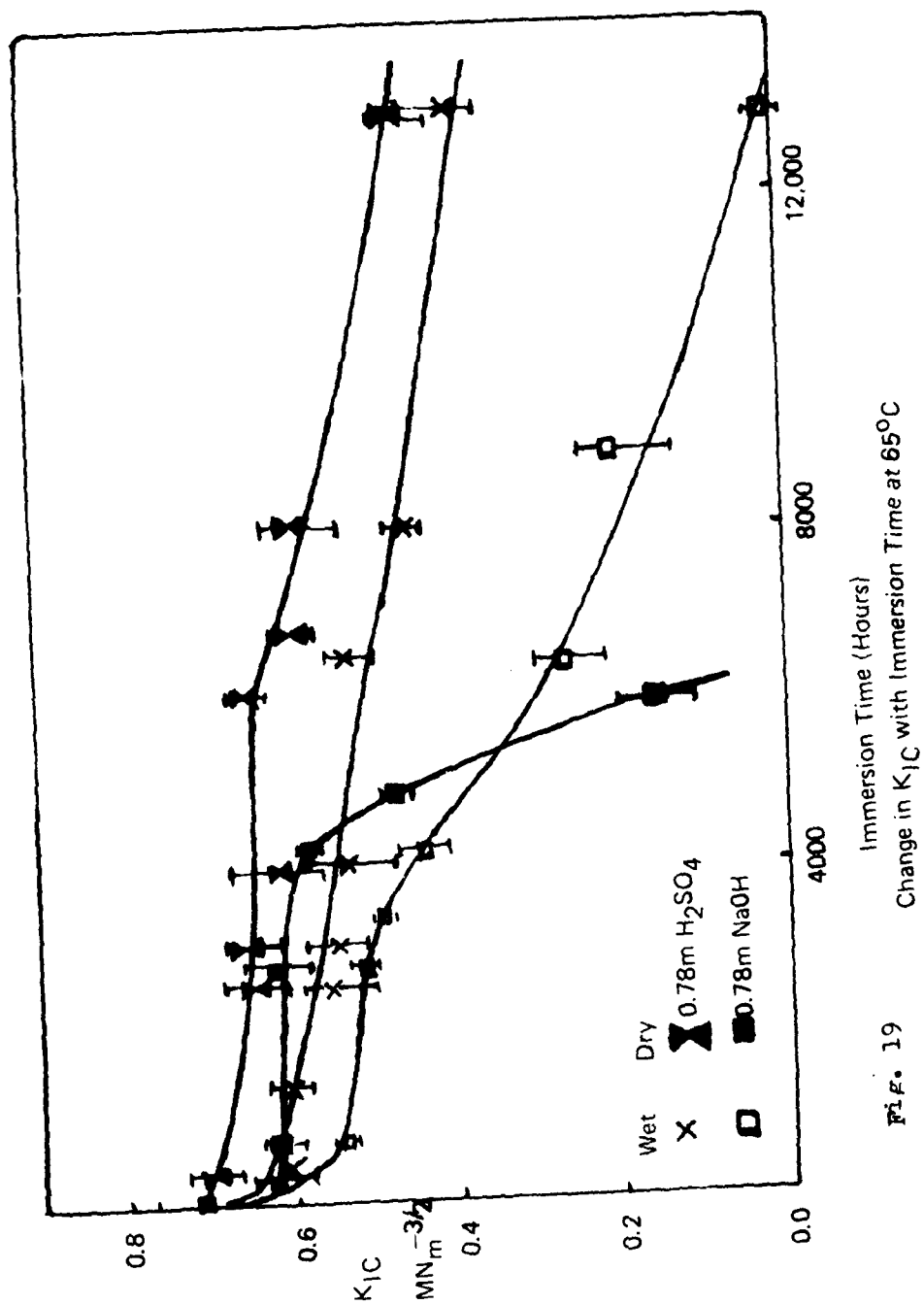


Fig. 19

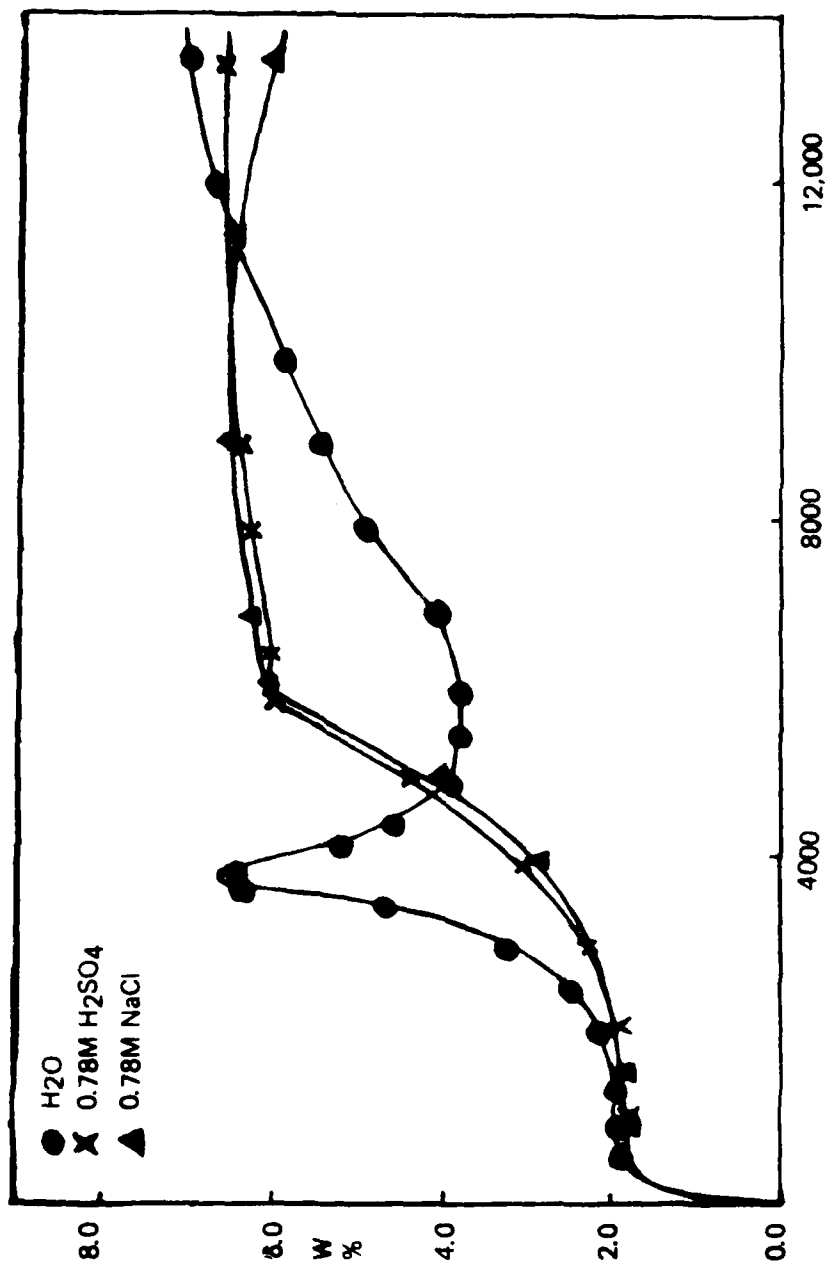


Fig. 20 ! Weight of liquid absorbed W with immersion time at 65°C

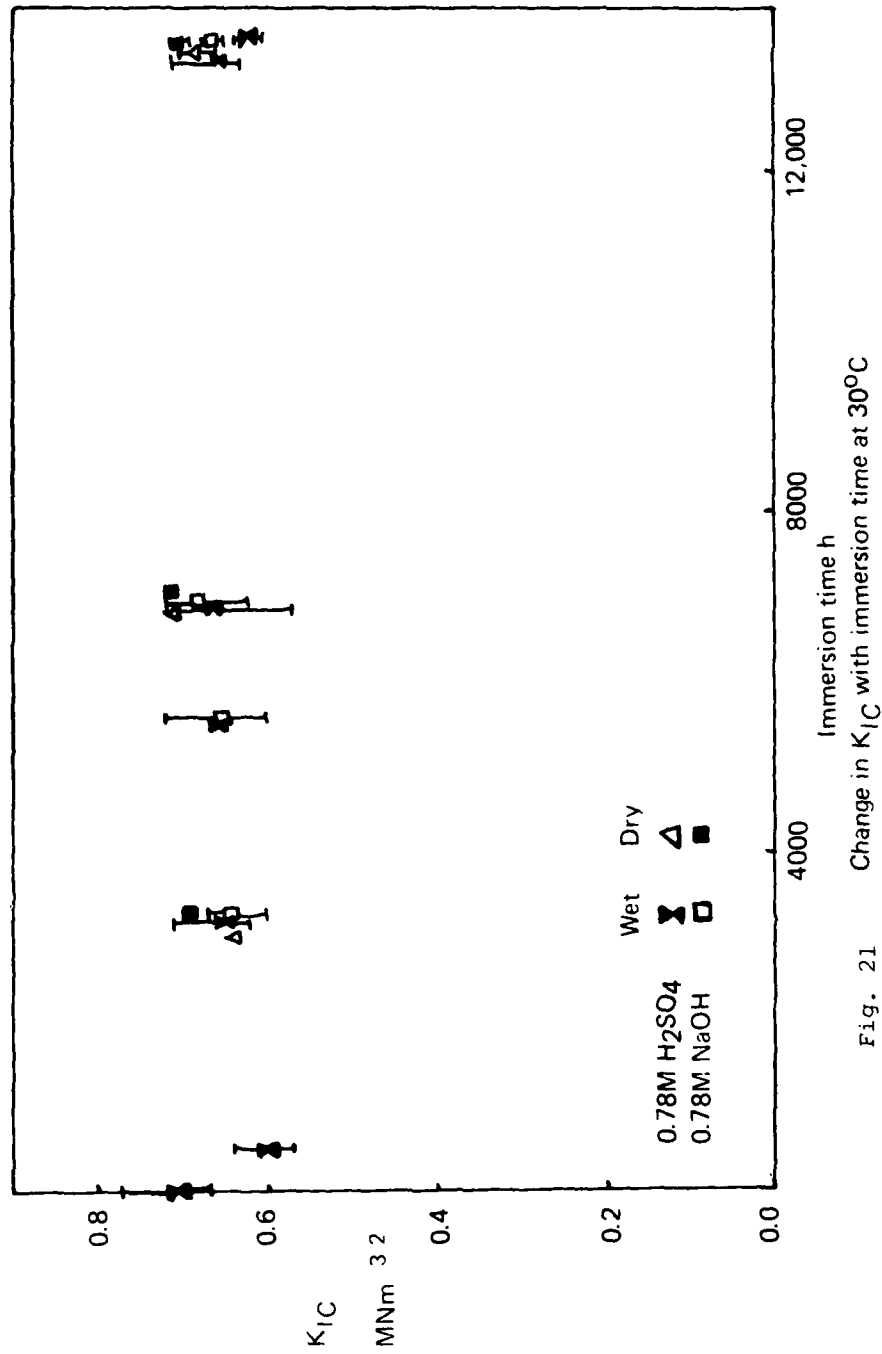


Fig. 21 Change in  $K_{IC}$  with immersion time at 30°C

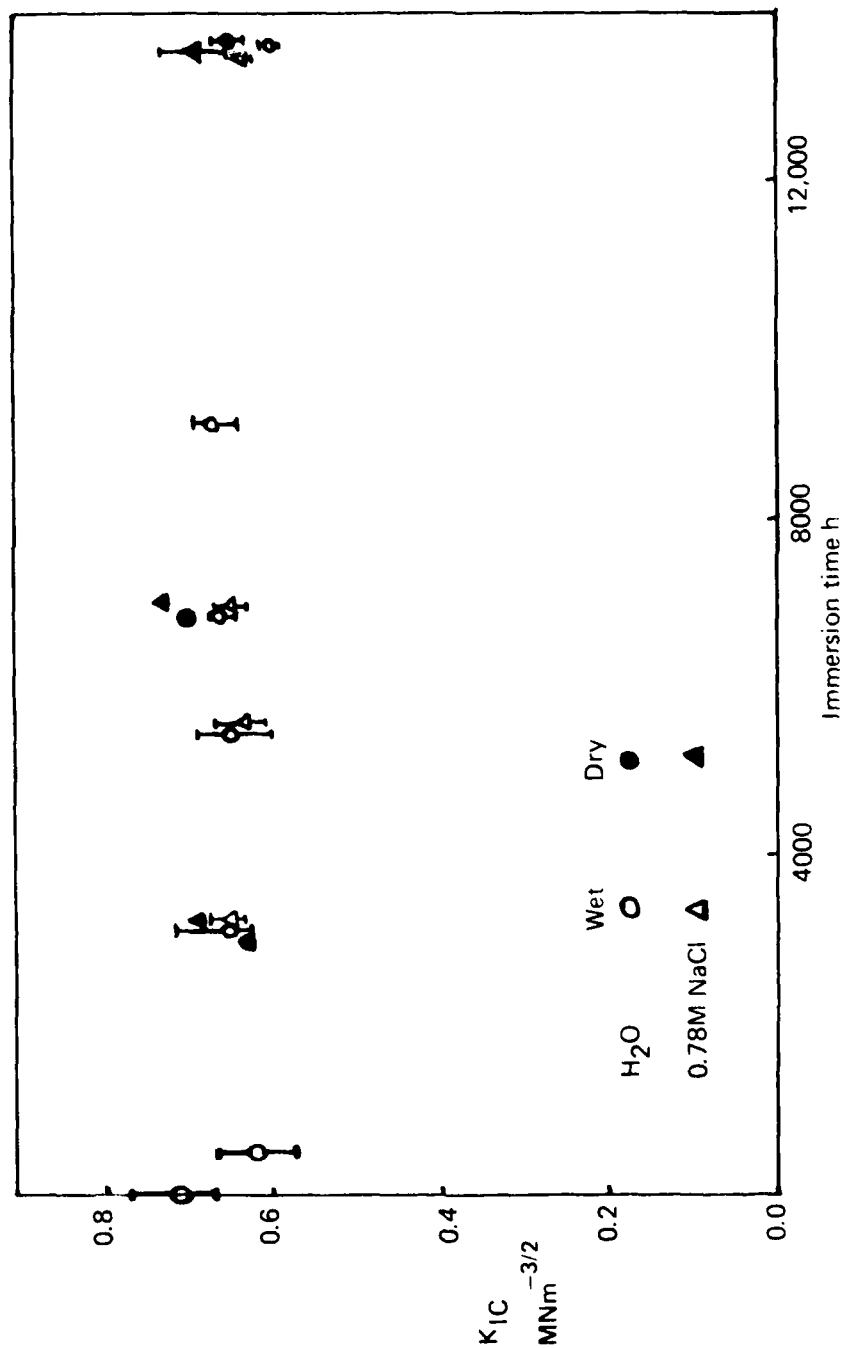


Fig. 22 Change in  $K_{IC}$  with immersion time at 30°C



molecular flow and crazing. There was, however, no evidence for this in the highly cross-linked epoxy systems.

The fracture surfaces of polyesters with different flexibiliser additions, and consequently, different degrees of cross-linking, were associated (28) with stable crack growth, slow unstable crack growth and fast unstable crack growth. Regions of surface roughness, which could be differentiated, were found in regions of stable crack growth and fast unstable crack growth and smooth surfaces in regions where slow unstable crack growth occurred. The formation of similar surface roughness was observed in an epoxy resin (29) and associated with stable crack growth and tentatively attributed to the existence of a large plastic zone ahead of the crack tip.

When cross-linked polymers are fractured above the glass transition temperature, the general correlations found for fracture surface characteristics obtained below the glass transition temperature are reversed. In particular, the amount of surface roughness is found to correlate well with the mechanical loss, or hysteresis, of the material rather than with the crack propagation rate.

#### 2.5 Water resistance of polyesters in general

Polyester resins are not seriously affected by cold water, but they are rapidly degraded by boiling water and steam. Many accelerated tests are carried out at temperatures much higher than those which the material was ever intended to withstand. Opinion is divided about whether acceleration by temperature is legitimate, or whether it introduces processes which could not normally occur at all.

The degradation process is believed to involve:

- (1) water absorption, causing swelling
- (2) leaching out of non-bound matter
- (3) hydrolysis of ester groups
- (4) further leaching of hydrolysis products
- (5) osmotically induced cracking

It has never been established whether the increased hydrolytic degradation found with low molecular weight resins is caused primarily by the large number of chain ends or by the likelihood of a larger weight fraction of leachable matter. End-blocking of the hydrophilic chain ends has been investigated, but the results were inconclusive (28).

#### 2.6 Resin structure, toughness and water stability

A study by Pritchard, Rhoades and Rose (20) led to the conclusion that the fracture toughness of polyester resins was inversely related to the maleic:phthalic molar ratio, R, where R was varied between unity and infinity. In most commercial resins, however, the ratio is between 0.5 and 2.0.

During the synthesis of these resins, it was noted that high maleic:phthalic ratios were associated with high losses of glycol, either by evaporation or as a result of side-reactions. Consequently, extra glycol had to be used for these resins, in order to complete the reaction. The precise quantity of glycol affected the chain length distribution and the fracture toughness.

The existence of low molecular weight components would be expected to facilitate viscous flow and increase the work of fracture. Therefore the toughest polyester resins should have a fairly low cross-link density (low maleic:phthalic ratio) and a significant molecular weight "tail". However, water resistance would be adversely affected by this "tail". The absorption of water should be reduced by a low maleic:phthalic ratio, since this introduces hydrophobic aromatic groups. There must be a minimum value of R, below which the resin becomes a soft gel, with toughness falling to a low level. This range of R values does not seem to have been explored.

## 2.7 Molecular weights and molecular weight distributions

Using the conventional terminology,

$M_n$  = number-average molecular weight

$$= \frac{\sum N_i M_i}{\sum N_i} = \sum \bar{N}_i M_i$$

and  $M_w$  = weight-average molecular weight

$$= \frac{\sum N_i M_i^2}{\sum N_i M_i} = \sum \bar{W}_i M_i$$

where  $N_i$  = number of molecules of mass  $M_i$  and  $\bar{N}_i$ ,  $\bar{W}_i$  refer to the number-fractions and weight-fractions having mass  $M_i$  respectively, we need to know for each resin the values of  $M_n$  and the degree of dispersity,  $M_w/M_n$ . It is also important to know the molecular size distribution to assess the size of the "tail".

$M_n$  is usually determined by vapour pressure osmometry and the size distribution by gel permeation chromatography. If the size distribution indicates the presence of a large tail, this can be removed by fractionation.

The relationship between molecular size and molecular weight distribution is determined by calibration methods, normally based on polystyrene. The value of the dispersity for a polyester can be estimated by using an expression such as

$$\frac{M_w}{M_n} = \left( \frac{1 + a'}{1 + a} \right) \cdot \left( \frac{M'_w}{M'_n} \right)$$

where  $a$ ,  $a'$  are the Mark-Houwink "a" constants for polyester and polystyrene respectively, and

$$\frac{M'_w}{M'_n}$$

is the dispersity indicated by the G.P.C. data for polystyrene. However, the above expression can only represent an approximation for such polymers as polyesters. The value of  $a$ , for example, may not be the same for all polyester resins. Most polymers have a value between 0.5 and 1.0; in a large number of cases,  $a \approx 0.7$ . It will be assumed in this work that all the polyester resins used have the same value of  $a$ . The value of  $M_w/M_n$  will thus be directly proportional to the value of

$$\frac{M'_w}{M'_n}$$

which is obtained by G.P.C. with the same constant of proportionality for each polyester. Direct determination of  $M'_w$ , e.g. by light-scattering, would enable absolute values to be calculated for

$$\frac{M_w}{M_n}$$

and for  $a$ .

It should be clear from the context whether  $a$  refers to molecular size constants or to crack length.

### 3. EXPERIMENTAL PROCEDURES

#### 3.1 The isophthalic programme

##### 3.1.1 Resin description

A single batch of polyester resin was manufactured by Synthetic Resins Ltd. of Liverpool, using the formulation:

isophthalic acid,	1 mole
maleic anhydride,	1 mole
propylene glycol,	1 mole
diethylene glycol,	1 mole

The manufacturers supplied the following data:

Hydroxyl value (by acetylation)	34.5
Acid value	26.6
Volatile matter ( $W/W$ )	41.5%

The number-average molecular weight was found to be 1827 and the weight-average molecular weight to be 4114.

The maleate-fumarate isomerization was estimated as 74%.

The heat distortion temperature (B.S.2782,1026) was 79°C.

The G.P.C. curve is given in Figure 4.

### 3.1.2. Fracture toughness measurement

The resin was cast into sheets by a carefully standardized method and the sheets machined to give centre-notched fracture toughness specimens (see Figure 5).

The fracture toughness was determined by breaking the samples in tension at a constant crosshead rate of 1 mm/min., using an Instron 1114 machine. A typical load-deflection curve is shown in Figure 6. The value of the critical stress intensity factor,  $K_{IC}$ , was calculated by means of the equation (31)

$$K_{IC} = \frac{Pa}{BW} \left[ 1.77 + 0.227 \left( \frac{2a}{W} \right) - 0.510 \left( \frac{2a}{W} \right)^2 + 2.7 \left( \frac{2a}{W} \right)^3 \right]$$

where

- P = maximum load
- 2a = crack length
- W = specimen width
- B = specimen thickness

The necessary crack tip radius was determined by plotting the calculated value of  $K_{IC}$  against the square root of the tip radius (Figure 7).  $K_{IC}$  was measured at two strain rates

(Figure 8) to test its strain rate sensitivity and also with various specimen thicknesses (Figure 9). Standardised post-cure times were evolved, i.e. 3 hours at 80°C after 24 hours at ambient temperature. Changes in  $K_{IC}$  with post-cure time were recorded (Figure 10).

The applicability of linear elastic fracture mechanics to the resin was tested by plotting  $\sigma^2 Y^2$  against  $1/a$ , where

Y = the expression in square brackets in the previous equation

This was performed both for the resin as supplied, and also after immersion in water at 65°C for 3000 hours. (See Figures 11-12).

### 3.1.3. Immersion in water and aqueous liquids

Fracture toughness specimens were immersed in the following liquids at 65°C and at 30°C

- distilled water
- 0.78M sulphuric acid
- 0.78M sodium hydroxide
- 0.78M sodium chloride
- 2M sodium chloride

The notch tips were sharpened after immersion.

The following properties were measured as a function of immersion time:

- critical stress intensity factor
- mass
- length
- plastic zone radius ( $r_y$ )

The values of  $r_y$  were computed from the equation

$$r_y = \frac{K_{IC}^2}{6\pi\sigma_y^2}$$

and  $\sigma_y$  values were obtained by compressing blocks (3.5 x 3.5 x 7.0 mm) at 1 mm/minute. The compression modulus was obtained at the same time.

Values of mass and of  $K_{IC}$  were found both from "wet" specimens which had simply been surface-wiped with a tissue and also from "dry" specimens which had been dried to constant weight at the immersion temperatures.

### 3.1.4. Microscopic examination (before fracture)

Optical microscopy was used to check crack tip radius and also to observe whether crack blunting occurred if any crack tips were sharpened before immersion. Specimens were periodically examined to check for the formation of osmotic disc cracks. It was noted whether these cracks lay in the path of the intended propagation route.

### 3.1.5. Fractographic examination

Fracture surfaces were examined by means of a Cambridge 610 scanning electron microscope. Samples for examination, approximately 15 x 15 mm, were cut from the fracture toughness specimens and mounted on standard stubs. A thin film of gold was deposited on the specimens, using a Polaron sputter-coater, to prevent electrostatic charging.

Optical microscopy has also been used to examine the fracture surfaces, using samples which have been immersed for various periods.

## 3.2 Orthophthalic programme

### 3.2.1 Plan

This programme is at an early stage. The work falls into the following main categories:

- (a) Resin synthesis
- (b) Resin analysis and characterization
- (c) Fractionation of the resins into narrow molecular weight bands
- (d) Blending of fractions to produce resins of desired molecular weight distributions, so as to compare
  - (i) resins of the same or similar  $M_n$ , but different distributions
  - (ii) resins of similar range of chain lengths, but different  $M_n$
- (e) Production of fracture toughness specimens
- (f) Measurement of the same properties listed in Section 3.1.3 above, after immersion in water at 50°C. (The lower temperature was chosen because the heat distortion temperature of the resins was lower than that of the isophthalic resin).
- (g) Production of resins with the hydrophilic chain ends blocked by chemical blocking agents, to observe the effect on the hydrolytic stability. (32)  
[Orthophthalic rather than isophthalic resins were chosen for this section of the work because (a) they are much more widely used commercially, (b) they are made by a single stage synthesis, which simplifies the preparation and might improve reproducibility]

### 3.2.2 Progress

Six orthophthalic resins have been prepared "in-house" using the nominal formulation

phthalic anhydride	1 mole
maleic anhydride	1 mole
propylene glycol	1 mole
diethylene glycol	1 mole

The starting materials were heated in 2 litre glass flange pots fitted with stirrer, condenser, receiver, nitrogen inlet and nitrogen flowmeter. 100 ppm inhibitor (p-tertiary butyl catechol) was added at the beginning and the reaction mixture maintained at  $190 \pm 4^{\circ}\text{C}$  with a nitrogen flow rate of  $460 \pm 20$  ml/minute. After 5 hours, acid value was periodically monitored by titration of samples with potassium hydroxide. At a pre-determined acid value, heating was stopped. A further 100 ppm inhibitor was added. When the temperature was  $80-100^{\circ}\text{C}$  a sample of resin was removed for analytical purposes. Styrene crosslinking agent was added carefully with stirring.

The quantities of glycol added were not precisely those in the nominal formulation; resins were prepared with 2% and with 5% excess of each glycol, to allow for losses.

Characterization of these resins is proceeding; the methods are as follows:

<u>acid value</u>	- by titration of 2.0 g of the resin with 0.1M methanolic potassium hydroxide
<u>hydroxyl value</u>	- by acetylation with acetic anhydride
<u><math>M_n</math></u>	- by vapour pressure osmometry, using a dioxane solution
<u>Molecular weight distribution</u>	- by gel permeation chromatography in tetrahydrofuran solution at $25^{\circ}\text{C}$
<u>Viscosity</u> (of styrene solution)	- by Ferranti concentric cylinder viscometer, at a shear rate of $13 \text{ sec}^{-1}$
<u>Solids content</u>	- by heating for one hour at $150^{\circ}\text{C}$
<u>Heat distortion temperature</u>	- by BS 2782 (102 G)
<u>Maleic-fumaric isomerization</u>	- by N.M.R.

#### 4. RESULTS AND DISCUSSION

##### 4.1 Introduction

The following account applies only to the isophthalic programme. The results of the orthophthalic work, mentioned in the previous sections, and funded in part by the U.S. Army, will become available later.

The importance of the isophthalic programme is that it establishes a baseline description of how a commercially produced high performance polyester resin is affected by prolonged water immersion. The subsequent orthophthalic work, incorporating minor variations in resin structure but only within an unchanging nominal formulation, will indicate whether more precise control of resin synthesis and quality assurance would be beneficial in the context of fracture toughness, water stability and retention of mechanical properties.

Carrying out prolonged immersion tests below the heat distortion temperature is a more certain guide to resin behaviour than using accelerated tests in, for example, boiling water, because the validity of extrapolations from high temperature has not yet been established. It is notable that Kaelble and Dynes (9) found a very large and substantially irreversible reduction in the fracture toughness of an epoxide resin after boiling in water for only 132 hours (Figure 13). Water never produced such a harmful effect on the isophthalic resin described here, even after 15,000 hours at 65°C. This is despite the known water vulnerability of polyesters (compared with epoxides).

##### 4.2 The validity of applying linear elastic fracture mechanics to polyester resins

Figures 11 and 12 both show the relationship between  $\sigma^2 Y^2$  and  $1/a$ . (It was considered important not to assume that because the relationship was linear for unimmersed samples, it would still be so after modification by water immersion). In fact straight lines were obtained in both cases. The radius of the assumed plastic zone,  $r_y$ , was calculated to be 1.51  $\mu\text{m}$  for the unimmersed resin, and this  $r_y$  approximately doubled after immersion in water at 65°C for 13,000 hours. However, drying the resin completely reversed this increase (see Table 1).

Larger increases in  $r_y$  were observed in 0.78M NaCl, and still larger ones in 2M NaCl ( $r_y = 16.43 \mu\text{m}$ ) but drying always caused reversion to a low value. It was found that the increases in half crack length,  $a$ , (obtained by correcting for plastic zone radius, i.e. using  $a + r_y$  instead of  $a$ ), did not affect  $K_{IC}$  significantly, since  $K_{IC}$  converged to the experimentally derived values immediately. So the irreversible work at the crack tip has little influence on the overall work of fracture and linear elastic fracture mechanics can be applied to both



control and immersed resins. The value of  $K_{IC}$  derived from Figure 11 was found to be in good agreement with that  $K_{IC}$  estimated from stress intensity factor curves for centre-notched rectangular sheets under uniaxial tension, given by Rooke and Cartwright (33).

#### 4.3 Specimen dimensions

There was no difference between the  $K_{IC}$  values obtained using 20 x 80 mm and those obtained using 30 x 120 mm specimens. The smaller ones were adopted for convenience. The diameter of the central hole had no effect within the range 0.9 to 2.0 mm. Figure 9 shows that thickness was unimportant between 1.1 and 7.0 mm. This was further confirmed by a t-distribution test. The specimen dimensions were sufficient to provide plane strain conditions, i.e.

$$a; \frac{W}{2-a} ; B \geq 2.5 (K_{IC}/\sigma_y)^2$$

Figure 7 shows that a maximum notch tip radius of 0.01 mm was required to achieve values of  $K_{IC}$  independent of tip radius variability. Microscopic inspection shows that the radii actually achieved in this project were of the order of 0.5  $\mu$ m or less. However, if crack tips were sharpened before immersion, the ones in sodium hydroxide were blunted. For this reason sharpening was carried out after immersion.

#### 4.4 The effect of heat on $K_{IC}$

Immersion in hot water subjects a resin to two influences: heat and water. The resin samples were therefore heated at 65°C in the dry state to observe whether this alone altered  $K_{IC}$ . The samples were very slowly cooled before any measurements were made. It was found that a very short period of heating (ca. 15 minutes) reduced  $K_{IC}$  from 0.71 to 0.60  $\text{MNm}^{-3/2}$ , but that the original value was gradually restored if heating continued for several thousand hours. These results were explained in terms of an initial increase in free volume followed by a low free volume equilibrium state. The compression modulus was lowered, after 15 minutes heating, by about 5%. The modulus later recovered, partly because of free volume changes. However, the loss of up to 0.5% mass by evaporation of volatile matter would also contribute significantly, raising  $K_{IC}$ .

If left at ambient temperature, specimens still lost a little volatile matter and  $K_{IC}$  increased from 0.71 to 0.75  $\text{MNm}^{-3/2}$  over 1300 hours.

Further crosslinking could take place if heating took place above the original postcure temperature.

#### 4.5 Disc crack generation

The term "disc crack" is used to describe rather flat, approximately circular internal cavities forming in the fracture toughness specimens after prolonged immersion in aqueous liquids. The origin of these cracks is believed to be the osmotic pressure generated by water-soluble impurities in the resin. Since the mechanism is osmotic, the generation of disc cracks is slowed down in concentrated solutions of electrolytes such as sodium chloride. White deposits are sometimes found in disc cracks. Ashbee, Frank and Wyatt thought that the impurities responsible were traces of inorganic matter (34). It was found, however, in this programme that dosing the isophthalic resin with 1% finely powdered sodium chloride did not produce earlier or larger disc cracks than normal. In fact they were only about 50 $\mu$ m across instead of the usual 300 to 700 $\mu$ m. Addition of excessive inhibitor had no effect. But addition of quantities of free glycol to the resin between synthesis and crosslinking produced a twentyfold reduction in the time necessary to generate disc cracks (100 hours instead of 2000 at 65°C). Furthermore, if the cured resin were subjected to vacuum desiccation at ambient temperature, so as to reduce the level of free glycol, the tendency to form disc cracks was reduced.

When samples of resin were boiled in water containing 1% of each of the two glycols, the samples were attacked at the surface and quickly fragmented.

The disc cracks took longer to appear in dilute aqueous solutions of sodium chloride and in sulphuric acid than in water, as expected. Moreover the distribution was different: there were only a few, randomly orientated cracks within 0.2 mm of the sample surfaces, but more in the central core, where they were preferentially aligned parallel with the major flat surfaces of the specimens (because of swelling stresses induced by absorption). More concentrated, 2M sodium chloride produced no cracks for 7000 hours and even then, none formed within 0.9 mm of the surfaces. The absence of surface-region cracks was tentatively ascribed to the fact that there was time for water-soluble impurities in the resin to diffuse out.

Immersion at 30°C produced only a few 40 $\mu$ m cracks close to the surfaces of specimens. This may have been because much longer timescales were required at this temperature.

Model experiments were carried out with drill holes for simulated disc cracks, to determine their effect on the measured values of  $K_{IC}$ . There was no effect if the simulated cracks were fairly remote from the tip, but if they were almost touching it, a significant lowering occurred. This was because the strain energy fields between the main crack and the disc cracks began to overlap. However, if the disc cracks actually touched the tip,  $K_{IC}$  apparently rose very sharply, indicating that the tip radius had been increased.

As cracks become more numerous, intercrack spacing becomes less than the crack diameter and overlapping of strain energy fields occurs. Using Sneddon's expression (35) for a disc-shaped crack (not a through crack) in an infinite solid

$$a_i = \frac{K_{IC}^2 \cdot \pi}{4\sigma^2}$$

the inherent flaw size  $a_i$  was estimated with the aid of unnotched, polished tensile specimens. Table 2 shows the estimated values compared with observed disc crack sizes. The fact that, as immersion time increased, the estimated dry value exceeded the observed values, indicates that interaction between cracks took place after a time. (The estimated wet value was always substantially greater than either the observed wet value or the estimated dry value. This may be because of interaction of the osmotic pressure in the cracks with the stress fields around them).

#### 4.6 Hydrolysis

Hydrolysis of polyesters is the reverse of their synthesis and occurs to a small extent when the resins are heated for long periods in water. Probably acid-catalysed hydrolysis is less deleterious than base-catalysed hydrolysis, since the latter process forms a resonance-stabilized carboxylate anion which has little tendency to react with glycol and revert to polyester. Consequently, hydrolysis in alkaline media is irreversible. This is evident in the very large loss of weight caused by immersion in alkali (Figure 14) compared with that in the other liquids (Figure 15). In all the liquids, the total loss of weight of specimens (after drying out) was greater than the 2.4% lost by solvent extraction of finely divided samples immersed in chloroform. Therefore all the aqueous liquids induced some hydrolysis, increasing the leachable components. But sodium hydroxide produced far the most extensive hydrolysis and it was possible to deduce from samples immersed in it what the effects of hydrolysis were. Severe attack on the surfaces led to layers of hydrolysed resin peeling off. The residue was washed, dried and examined. It did not burn, which suggested a high inorganic (sodium) content.

White deposits in the disc cracks were collected and analysed. The melting point was  $340^\circ\text{C}$  and the infrared and N.M.R. evidence identified the deposits as isophthalic acid. These deposits were found even when the resin was immersed in sodium chloride, although the rate of uptake of water into the samples and the subsequent development of cracks and hydrolysis products decreased with increasing salt concentration.

Immersion at 30°C produced an almost negligible reduction in dry weight over a period of 13,000 hours, except in sodium hydroxide, when a small amount of hydrolysis took place. (Figure 16)

#### 4.7 Changes in fracture toughness

The fracture energy of a polymer glass depends on the extent of viscous deformation during failure, whether caused microscopically by crazing or shear banding, or macroscopically by necking. The changes taking place in polyester resins during immersion in hot water are in some ways hostile to, and in other ways favourable to, viscous flow. Simple swelling and plasticization by water uptake favours it; leaching out of the low molecular weight "tail" opposes it; hydrolysis greatly enhances it, while the generation of disc cracks has little effect until they begin to interfere with crack propagation from the main notch, when the situation is as previously discussed in Section 4.5.

From equations (6) and (7),  $K_{IC}$  depends on both  $\gamma$  and  $E$ . Enhancement of flow increases  $\gamma$ , but reduces  $E$ ; hydrolysis reduces the crosslink density and so reduces  $E$ . The value of Poisson's ratio should not be very greatly affected (24). The change in  $K_{IC}$  depends on whether the probable increase in  $\gamma$  outweighs the reduction in  $E$ . The following evidence suggests that, as hydrolysis proceeds, it becomes more dominant, with a consequent reduction in  $E$  and  $K_{IC}$  at long immersion times.

Figure 17 shows how the fracture toughness changed as a result of immersion in water and in sodium chloride, at 65°C. There was not much difference between the two liquids. After about 7,000 hours, the value of  $K_{IC}$  (wet) had fallen considerably in both liquids, but it was restored on drying out. Water plasticization was assumed to be the main factor at this stage. Later,  $K_{IC}$  (wet) fell still further, and the amount of reversibility declined. This was assumed to be due to hydrolysis and permanent damage.

Figure 18 shows the change in net weight (i.e. the change resulting from the additive effects on sorption and leaching) of the undried specimens, as a function of immersion time at 65°C. Water entered the resin more slowly in the presence of solute ions, regardless of whether they were from sodium chloride or sulphuric acid. Consequently, disc crack development was delayed. Eventually, however, the solutions produced peak values almost as great as those produced by distilled water. The peak values followed the onset of disc crack formation and were followed in turn by hydrolysis, with decreases in net weight. The disc cracks were found to contain hydrolysis products.

The changes caused by dilute sodium hydroxide (not shown) were much more drastic, with 100% increase in net weight after less than 8,000 hours. After 6,000 hours, drying tended to reduce  $K_{IC}$  still

further instead of partially restoring it. By 7,000 hours, the measurement of  $K_{IC}$  had become impossible with dried specimens. (Figure 19).  $K_{IC}$  Sulphuric acid did not have this effect, because hydrolysis in acid is reversible.

(Figure 20 illustrates the fact that, although net weight change eventually declines, the weight of sorbed water does not follow a simple path, but eventually rises again).

The mere absorption of water is not responsible for serious embrittlement, but when disc cracks form, water uptake accelerates, and so does hydrolysis. The whole process is slower at 30°C. (See Figures 21, 22).

It has often been observed in this laboratory that polyester resins differ in their tendency to form disc cracks. It seems important that the generation of these disc cracks should be suppressed and one relevant factor may be the quantity of free (unreacted) glycol in the resin.

Another general observation is that polyester-glass laminates do not undergo very serious disc cracking, although a few cracks do form and they become much more numerous if the laminate is exposed to very high temperatures. It may be that the glass fibres restrain the resin and prevent it from experiencing high local stresses. If the generation of disc cracks is a factor accelerating hydrolysis, as seems likely, then laminates will probably be affected to a much lesser extent than cast resins by hot water immersion.

#### 4.8 Fractographic observations

For exposures of up to 1500h in distilled water, 2000h in 0.78M sodium hydroxide, 3000h in 0.78M sodium chloride and 7000h in 2M sodium chloride at 65°C, the fracture surface characteristics of polyesters are similar to those reported by Owen and Rose (28) for room temperature unexposed material. Quantitatively, the extent of the different fracture characteristics as a function of immersion time has still to be investigated. At longer exposure times, disc cracks are formed within the polyester and they dominate the structure of the fracture surfaces. This work is still proceeding.

### 5. CONCLUSIONS

(a) The report provides evidence that an unreinforced polyester resin of the isophthalic (i.e. relatively water-resistant) variety undergoes considerable loss of toughness after a little under two years in hot water. Only slightly different effects were found in 0.78M sulphuric acid and sodium chloride. In sodium hydroxide, the resin was virtually destroyed.

(b) The mechanism was believed to be (1) water uptake (2) leaching of originally present non-bound substances (3) osmotic disc crack generation (4) hydrolysis, especially at surfaces and at disc crack sites (5) increasing loss of toughness as crosslink density fell and hydrolysis products were deposited. The generation of disc cracks was found to be related to free glycol content.

(c) The preparation of a series of conventional orthophthalic polyester resins is under way, the object being to determine optimum molecular weight distributions for hydrolytic stability. This work will be reported subsequently. The two programmes (orthophthalic and isophthalic) are complementary, in that the results obtained from one are expected to be relevant to the other.

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TABLE 1

Compressive yield stress  $\sigma_y$  and plastic zone radius  $r_y$  of the resin

unimmersed resin							
Immersion time h.		$\sigma_y$ MNm <sup>-2</sup>		$r_y$ $\mu$ m			
		$\sigma_y$	$r_y$	$\sigma_y$	$r_y$	$\sigma_y$	$r_y$
		MNm <sup>-2</sup>	$\mu$ m	MNm <sup>-2</sup>	$\mu$ m	MNm <sup>-2</sup>	$\mu$ m
13,600 at 30°C		104.0	1.77	111.9	1.63	109.4	1.82
13,000 at 65°C wet		60.1	2.97	51.1	3.09	50.2	3.71
dry		106.0	1.33	91.5	1.28	100.0	1.17
						-	-

2M NaCl 65°C		2M NaCl 65°C		6M H <sub>2</sub> SO <sub>4</sub> 65°C	
7354h		13,000h		9928h	
$\sigma_y$	$r_y$	$\sigma_y$	$r_y$	$\sigma_y$	$r_y$
MNm <sup>-2</sup>	$\mu$ m	MNm <sup>-2</sup>	$\mu$ m	MNm <sup>-2</sup>	$\mu$ m
wet 66.3	11.1	46.6	16.43	129.6	1.21
dry -	-	104.0	1.13	-	-

TABLE 2

Inherent flaw size in H<sub>2</sub>O at 65°C

Immersion time h.	estimated $a_i$ $\mu$ m		observed $a_i$ $\mu$ m	
	wet	dry	wet	dry
2856	834	264	300	300
8100	2304	763	800	700
8950	2965	882	-	700
10,000	3133	-	800	700